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Determination of the Concentration of Pesticides in Atmosphere at High Altitudes after Aerial Application

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Information on the distribution of pesticides and their metabolites in the atmosphere is very important, since it influences the atmospheric environment. Volatilized pesticides have some possibility to rise to higher altitudes and to diffuse accompanied with ascending currents in the daytime.

Concentrations of pesticides in the atmosphere are usually measured at 1.5 m in height from the ground. However, those of pesticides at much higher altitudes or elevations have been rarely reported. DDT concentrations in the atmosphere at 750~2460 m in height were measured after aerial spraying over the forested area, where the maximum concentration of total DDT was about 800 m in height and it was 15 ng/cu m (Orgill et al. 1974). Atmospheric transports of chlorpyrifos, diazinon and parathion were measured after their spraying on orchards, whose concentrations in the atmosphere were determined in three places, at 114 m of elevation site placed 0.5 km away from the orchard field, at 533 m of elevation site (25 km away), and at 1920 m of elevation site (39 km away), respectively. Concentrations of pesticides in the atmosphere at 114 m in elevation ranged from 0.013 ng/cu m to 13 ng/cu m, those at 533 m were below the limit of quantification (0.0014 ng/cu m) up to 0.083 ng/cu m, and those at 1920 m were below the quantification limit (Zabik et al. 1993). Thus, pesticide concentrations decreased simply with increasing in altitude or elevation. Concentrations of 47 pesticides at 150~800 m in height on a paddy field were measured with GC/MS using SIM (Selected Ion Monitoring) method, and they were below the detection limits of 5 ~ 50 ng/cu m (Watanabe 1996a). In this paper, pesticide concentrations at several altitudes up to 100 m in height have been determined, and the disappearance of pesticides in the atmosphere at the surface of the ground has been investigated. Time decay of concentrations in the atmosphere on the ground has been also measured after the aerial application.

MATERIALS AND METHODS

Pesticides of pure grade were used as their standards which were obtained from the manufacturer of technical pesticides, and solvents of pesticide residue grade (Wako Pure Chemical Industry) were used.

Fenitrothion and fenobucarb were sprayed aerially over 300 ha of a paddy field at Sakura in Chiba Pref., at the rate of 450 g and 300 g a.i./ha, respectively, with helicopter at 10~12 m in flight height on Aug. 1, 1992. Spraying of pesticides was finished by 9:30. Sampling point "A" was placed inside the sprayed area, and four points, "B1", "B2", "C1", and "C2", were placed outside the sprayed area. Points "B1" and "B2" were located at 50 m east and west, respectively, from the boundary of the sprayed area. Point "C1" was located at 200 ~500 m west from the boundary line, and point "C2" was located at 700m northeast far from it. Sampling points were shown in Figure 1.

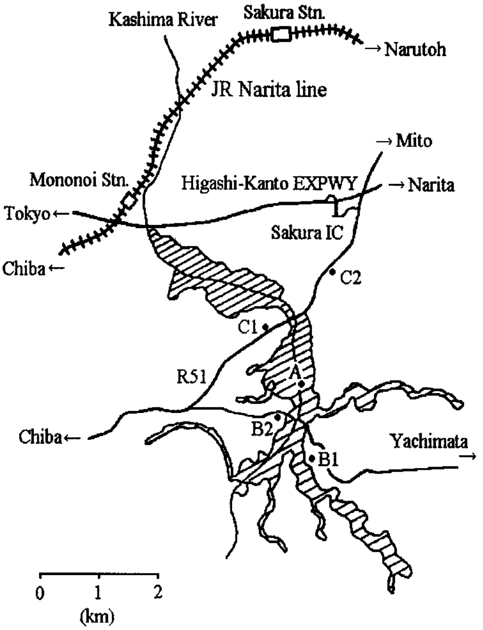

Figure 1. Map of sprayed area (under the Shadow of oblique line) and sampling points (A,B1,B2,C1 and C2).

Air was sampled at 1.5 m, 5 m, 30 m, 50 m, and 100 m in height on point "A" on the sprayed day. Silica gel cartridge columns (Waters Associates SEP-PAK SILICA) were bound to a pole at 1.5 m and 5 m in height. And 100 L of air was sampled with a few sets of silica gel columns and pumps (Shibata MP-601T) at the rate of 1.2 L/min for 30-40 minutes. Air volume was measured with a dry gas meter (Shinagawa-Seiki DK-2Cf-T). Four sets of silica gel columns and pumps with batteries were hung under the radio-controlled helicopter (Yamaha model R-50; body length 2.7 m and rotor diameter 3.1 m), and about 100 L of air at 30, 50 and 100 m in height were sampled with these silica gel columns at the rate of 1.2 L/min during a flight for 20 minutes over point "A". The altitude of radio-controlled helicopter was monitored by an altimeter and was controlled.

As monitors for the variation with elapsed time and with the horizontal distribution, 100 L of air at 1.5 m in height was sampled with silica gels at five sampling points, A, B1, B2, C1 and C2, between 13:00 ~ 14:00 during 5 days after the application.

Meteorological conditions, i.e., weather, temperature, relative humidity, wind direction and wind speed, were measured at point "A" and shown in Table 1. Meteorological parameters were observed at 1.5 m in height, so the wind speed (U: m/sec) at each altitude (Z: m) was estimated from the following equation,

Table 1. Meteorological conditions for air sampling
(1) August 1, 1992

	time				
	12:00-12:45	12:00-12:45	10:00-10:20	10:30-10:50	11:10-11:30
sampling altitude	1.5m	5m	30m	50m	100m
weather*	cloudy	cloudy	cloudy	cloudy	fine
temperature (℃)*	32	32	31	31	33
wind direction*	E	E	NE	NE	NNE
wind speed (m/sec)*	1.0	1.0 (1.3)**	1.0 (1.8)**	1.5 (3.0)**	1.5 (3.5)**

* : Meteorological conditions were observed at 1.5 m in height.
* * :Values of wind speed in the corresponding altitudes were estimated by eq. 1.

(2) August 1~6, 1992

date	elapsed days	weather	temperature (°C)	humidity (%)	wind direction	wind speed (m/sec)
1992. 8.1	0	cloudy	31	66	SE	1.8
8.2	1	rainy	22	74	N	1.4
8.3	2	cloudy	23	75	NE	2.5
8.4	3	cloudy	25	62	E	2.2
8.6	5	fine	34	62	SW	1.2

All meteorological conditions were measured at 14:00.

using the wind speed ($U_{1.5}$) at $Z_{1.5}$ in height (1.5 m):

$$U = U_{1.5} X (Z / Z_{1.5})^{p}$$

Here, the value of a power parameter p was assumed to be 0.2 as usual for a flat condition (Yokoyama 1980).

Trapped pesticides in a silica gel cartridge column were eluted with 10 mL of acetone. The acetone solution was concentrated by evaporation with a rotary evaporator in a water bath at <30°C under a reduced pressure, dried by N_2 gas, and filled up to 0.5 mL with hexane. Then, the concentrations of pesticides were determined with computer-controlled GC/MS (SIM), which was set to the condition of GC given Table 2. M/Z values of pesticides for SIM were set to the most suitable ones with high sensitivity and low interference (Watanabe 1996a), as shown in Table 3. Standard in solutions of pesticides were diluted with hexane to the concentrations of 10, 50 and 100ppb.

Table 2. Gas chromatographic conditions for pesticide analysis

GC/MS	Shimadzu QP-5000
Column	J&W Scientific, capillary DB-1, id 0.25mm × length 30m, film thickness 0.25 μm
Column temperature	60℃ held for 1 min; heating at 25℃/min, 150℃ held for 1 min; heating at 5℃/min, 250℃ held for 25 min
Injector	splitless
Injection temperature	250℃
Interface temperature	250℃
Carrier gas	He, 100 kPa
Flow rate	6.5 mL/min (total), 1.8 mL/min (in column)
Line speed	41.3 cm/sec
Sample size	2 μL
Ion source	EI
Ion multi. volt	2.0 kV

RESULTS AND DISCUSSION

Recoveries of pesticides using silica gel cartridge column have been reported recently (Watanabe 1996b). The average value of recoveries on 55 pesticides from silica gel was 97.9% when they were eluted with acetone. The average of recoveries on 52 pesticides after passing 100 L of air was 96.8% except disulfoton and fenthion, which were decomposed by oxidation at their alkylthio groups (R-S-). The average of collection efficiencies on 31 gaseous pesticides was 96.7% with the exception of butamifos, dimethoate, phosmet and piperofos. Tricyclazole had too low sensitivity for GC/MS(SIM). Therefore, 48 pesticides except above mentioned 7 pesticides were determined in this paper. These

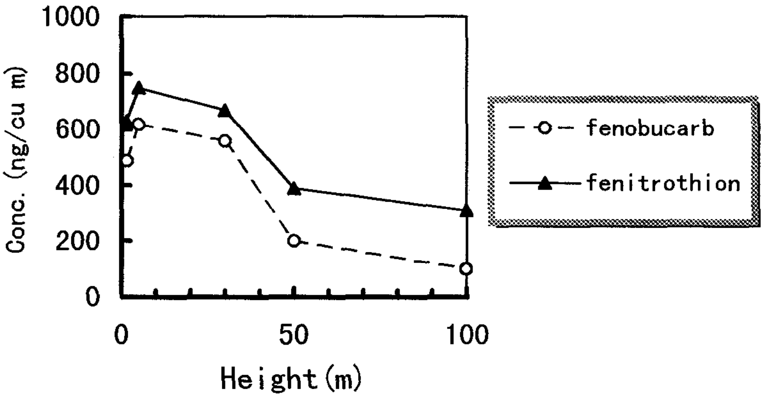

Figure 2. Concentration dependence of pesticides on altitudes on August 1, 1992

Table 3. Recoveries using silica gel, retention time, and M/Z of pesticides with GC/MS(SIM)

pesticides	recovery[a]			Rt[a]	M/Z			
	SILICA	AIR	C.E.		(1)	(2)	(3)	(4)
bifenox	92.9	—[b]	—	25.76	310	312	341	343
bromobutide	95.1	—	—	15.28	119	120	232	
buprofezin	96.5	102.1	90.5	21.07	105	172	190	
butachlor	107.1	91.4	93.5	20.06	132	237	238	
butamifos	96.4	97.4	49.5	20.03	96	200	286	
captan	93.8	—	—	18.02	149	151	264	
carbaryl	83.9	—	99.7	15.15	115	116	144	
chlorothalonil	87.3	93.2	94.1	13.49	229	264	266	268
chlorpropham	92.3	90.1	97.3	11.03	127	171	213	
chlorpyrifos	99.1	102.7	101.3	17.17	197	199	314	
chlorpyrifos-methyl	92.5	100.9	98.4	15.27	93	197	286	
diazinon	97.1	99.7	99.8	13.78	137	152	179	199
dichlorvos	110.4	—	—	5.66	109	185	220	222
dimepiperate	112.3	91.3	91.2	18.55	122	119	145	
dimetametryn	99.8	—	—	18.28	212	213	255	
dimethoate	97.5	96.3	60.2	11.88	87	125	229	
dimethylvinfos	94.4	93.3	79.2	16.88	204	295	297	
disulfoton	94.7	4.2	—	13.82	88	89	186	
edifenphos	100.4	100.4	75.9	22.22	173	201	310	
EPN	93.8	90.7	90.3	25.22	157	169	185	
etofenprox	99.8	—	—	34.57	107	135	163	
fenitrooxon	109.2	—	—	14.72	109	127	244	
fenitrothion	95.0	98.8	102.8	16.15	125	260	277	
fenobucarb	93.8	101.4	98.4	10.25	77	121	150	
fenthion	100.2	21.2	—	17.11	125	262	278	
fenthoate	98.1	97.6	102.5	18.65	125	157	246	274
fenvalerate(isomer A)	100.0	—	—	37.48	125	167	225	
fenvalerate(isomer B)	100.0	—	—	38.74	125	167	225	
flutolanil	99.2	—	—	20.15	145	173	281	
fthalide	88.4	—	—	17.11	241	243	270	272
iprobenfos	104.3	99.1	100.6	14.41	123	204	246	
isofenphos	98.7	93.6	88.4	18.74	213	245	255	
isoprocarb	85.3	102.3	102.8	9.10	121	136	193	
isoprothiolane	97.7	—	—	19.86	118	162	189	290
isoxathion	98.6	89.7	86.3	21.19	77	177	313	
linuron	104.5	—	—	16.39	160	187	248	
malathion	94.6	104.8	104.5	16.69	93	127	173	
mefenacet	105.9	—	—	26.81	120	148	192	
mepronil	108.4	—	—	22.51	91	119	269	
metaraxyl	96.7	—	—	15.75	192	206	249	
metolcarb	84.5	101.7	101.5	7.93	107	108	165	
molinate	104.0	89.9	97.2	9.17	83	126	187	
pendimethalin	95.1	100.5	98.2	18.32	162	192	252	
permethrin	106.3	—	—	29.98	163	165	183	184
phosmet	102.3	91.8	51.7	24.74	77	160	161	
piperofos	98.0	87.9	57.3	25.49	122	140	320	
pyridaphenthion	83.4	109.7	120.7	24.86	188	199	340	
pyroquilone	92.7	—	—	12.92	130	172	173	

Table 3. (continued)

pesticides	recovery [a]			Rt[a]	M/Z			
	SILICA	AIR	C.E.		(1)	(2)	(3)	(4)
simazine	108.8	98.2	99.1	12.24	173	186	201	
simetryne	103.8	87.8	97.1	15.26	155	170	213	
tetrachlorvinfos	102.2	104.9	90.7	19.56	329	331	333	
thiobencarb	94.9	89.8	100.4	16.69	100	125	257	259
tricyclazole	100.5	-	-	19.48	135	162	189	
trifluralin	103.3	90.9	94.4	11.82	264	290	306	
XMC	94.5	100.8	99.4	9.38	121	122	179	
xyrylcarb	92.5	99.1	101.4	9.95	121	122	179	
average	97.9 96.8[c]	92.1 96.7[d]	91.9					

a) SILICA: recovery from silica gel cartridge column (%). AIR: recovery after passing of air (%). C.E.: collection efficiency (%). Rt: retention time (min).
b): not measured.
c): average on 34 pesticides except disulfoton and fenthion.
d): average on 31 pesticides except butamifos, dimethoate, phosmet and piperofos.

pesticides were almost stable on silica gel below - 15°C except for disulfoton, thus their air sampled cartridges were stored at -20°C until the extraction.

The concentrations of some pesticides in the high altitudes of atmosphere at point "A" were shown in Figure 2. Fenitrothion and fenobucarb were clearly detected, since they were sprayed into the paddy field. Other 47 pesticides were determined but their concentrations were below 200 ng/cu m (fenitrooxon) , 100 ng/cu m (captan, bifenox and fenvalerate) or 50 ng/cu m (others) of the detection limit. The concentrations both of fenobucarb and fenitrothion were maximum at 5 m in height, because the center of pesticide plume was volatilized from rice plants in the paddy field and it was flowed around this height. The concentrations of fenobucarb at 30 m, 50 m and 100 m in height decreased to 1/1.1, 1/3 and 1/6 of its concentration at 5 m, respectively. The concentrations of fenitrothion at 30 m, 50 m and 100 m in height were decreased to 1/1.1, 1/2 and 1/2.4, respectively, of its concentration at 5 m. Therefore, the decreasing rate of concentrations of these pesticides were dependent on the altitude. The concentration ratios of fenitrothion to fenobucarb in the atmosphere were about 1.2 at 1.5~30 m in height, 2.0 at 50 m in height, and 3.1 at 100 m in height. Since the concentration ratio of fenitrothion to fenobucarb was 1.5 in a sprayed pesticide mixture, the composition of fenobucarb in the atmosphere at 1.5~30 m in height was increased more than that in the formulation itself. Because the vapor pressure of fenobucarb (19 mPa) was higher than that of fenitrothion (3.1 mPa), fenobucarb was easier to volatilize. However, the ratios of fenitrothion in the upper atmosphere at 50~100 m in height were larger than that in the formulation. The concentration of fenobucarb decreased significantly at the altitude higher than 50 m, while fenitrothion hardly decreased over 50 m. It was

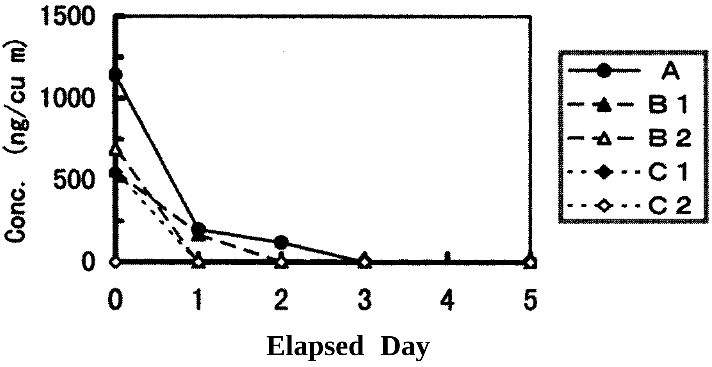

Figure 3. Concentration decay of fenitrothion in the atmosphere with the elapsed day

speculated that fenitrothion which had been sprayed over another area would be transferred into this survey area.

The concentration decays of fenitrothion and fenobucarb in the atmosphere at 1.5 m in height were shown with the elapsed day in Figures 3 and 4, respectively. Fenitrooxon, one of metabolites of fenitrothion, was 200 ng/cu m of its detection limit and it was not detected. The concentrations of fenitrothion and fenobucarb in the atmosphere at point "A" after the application were decreased to 18% and 15% after 1 day, to 10% and 9% after 2 days, to <8% and 6% after 3 days, and to <8% and 7% after 5 days, on compared with the concentration at the applicated day. The concentrations on the applicated day at points "B1" and "B2" (50 m away from the boundary line) were higher than that at point "C1" (about 500 m away). No pesticides were detected at points on the windward side. Therefore, the concentrations of pesticides were dependent both on the elapsed day and on the distance from the sprayed area. It has been reported that the concentrations of pesticides were dependent on the elapsed time, properties of pesticides, and meteorological conditions after the aerial spraying on forests or paddy fields

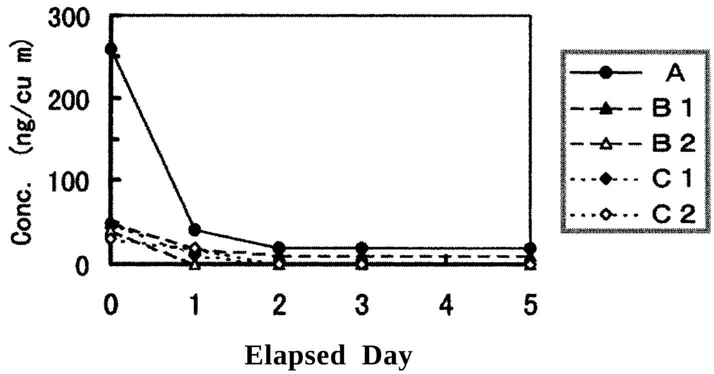

Figure 4. Concentration decay of fenobucarb in the atmosphere with the elapsed day

(Kawata et al. 1991, Kawata et al. 1994, Sundaram 1984). The results in this paper confirmed the previous observations.

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